HIGH PERFORMANCE CLEAR THERMOPLASTICS ELASTOMER

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Abstract

High performance clear TPE products are developed to replace silicone and PVC in various medical and personnel care applications. These are high clarity TPEs with high tensile and tear properties. They retain mechanical properties and dimensional stability after hours of testing in boiling water and repeated dishwasher cleaning cycles. These TPEs have good processability. They can be used in FDA and USP required applications.

Background

Silicone and PVC are widely used in medical and personnel care products requiring clarity . Silicone has excellent high temperature performance and chemical resistance. However, silicone is very expensive material. PVC is a low cost material with wide processing window exhibiting ocessing friendly together with high temperature properties. However, there is a growing recycling concern over PVC especially in Europe.

Styrene Block Copolymer (SBC) is a TPE that combine the processing characteristic of thermoplastics and physical properties of vulcanized rubbers. SBC compounds offer good economics and formulation flexibility meeting the end use performance requirements. Since the introduction of styrene block copolymer four decades ago, newer molecules with varied chemistry have been introduced to the market. Some of them have FDA and USP approval.

This paper concentrates on SBC compounds, which are intended for applications where silicone and PVC are presently specified offering improved economics over silicone and alleviating the recyclability concerns of PVC. We will first discuss the important design parameters that affect the clarity and properties of the TPE compounds. Specific examples will be highlighted to provide performance attributes.

Formulation Development

Based on the market feedback, the developmental TPE needed to meets three major general requirements;, clarity, heat resistance and softness. There are other properties requirements such as tensile, tear, creep, compression set, which are designed for functional performance.

Clarity

The clarity of compound is determined by refractive index of each ingredient and the resultant morphology. In addition, the surface smoothness of the molded part contributes to clarity. Ingredient selection for the TPE compound required a careful match of refractive indexes. Careful study of morphology and reduction of the difference of refractive index among the various ingredients leads to a material with improved clarity.

It is known that transparent polymer blend can be made of polymers with different refractive index provided the dimension of the dispersed phase is below the visual wavelength. One example is such a blend is SEBS with polypropylene (PP). PP is compatible with midblock of SEBS. Transparent or translucent compound can be made even though SEBS and PP have different refractive index. Low molecular weight SEBS and PP compound tends to give better clarity product than high molecular weight SEBS.

Appearance of finished product is affected by the smoothness of surface.. Surface smoothness of both injection molded and extruded products is affected by the rheology and interface shear stress of the system. A smooth surface can be achieved by using processing aid or special surface coated die to reduce the high shear stress. High molecular weight SBC is highly elastic and hence high shear stress is built at the surface even at very low shear rate. Processing aid is not very effective to improve the surface quality of the finished injection molded or extruded products.

The selection of SBC and rheology of the compound are the most critical to control surface smoothness of the finished product. Figure 1 shows the TEM of two of SEBS/oil/PP compound [(1)]. Styrene domain is stained black. The styrene domain of high molecular weight SEBS is less than visible wavelength. However, there is significant difference of appearance of the two compounds. The one with low molecular weight of SEBS is transparent and the one with high molecular weight SEBS is transclscent. It is difficult to make a judgement of clarity from the difference of morphology based on TEM pictures.

Service Temperature

DMA (dynamic mechanical analyzer) can be used to evaluate the service temperature. Test sample is clamped and strain-temperature relation under constant load is measured. For sterilization purpose, such as boiling water and autoclave, low stress loading can be used. For application at high stress and high temperature, a stress loading similar to application environment is preferred. Examples of typical DMA results are shown in Figure 2.

Hardness and modulus

Soft touch feeling is a combination of both hardness and modulus. Feeling of "softness" of two TPE of same hardness but different chemistry can be quite different, because of the difference of modulus. Examples are given later to show the difference of modulus of TPE of difference chemistry.

Mechanical properties such as tensile and tear are specified design requirement. Often there are more than one formula which satisfy these requirements. Two examples in Figure 3 show are shown to have similar tensile and elongation, while different in modulus. The sample with a lower modulus is felt softer than the higher modulus one.

SBC compound application

I. Silicone replacement for baby nipple

Majority of baby nipple/pacifier is made from silicone and natural rubber. Transparent SBC compound was developed, which has similar appearance as silicone rubber and mechanical properties necessary for nipple application.

The main requirements are listed in the following:

Transparency similar to silicone
Low hardness and low modulus
Good tensile and tear
Boiling water and dish washer
Abrasion and bite resistance
FDA direct fatty food contact approval

The properties are of silicone rubber and SBC compounds are compared in the following in Table I. SBC compound passed all the required testing. SBC compound was tested in boiling water for two hours. The mechanical properties change was found less than 5 percent and dimensional change is less than 2 percent. After normalized by ratio of specific gravity, SBC compound has a stronger tensile and tear strength than silicone based on weight. SBC compound is thermoplastics and can be recycled, which results in additional saving in processing cost compared with thermset silicone.

II. Silicone/PVC/TPV replacement for medical tubing

The plasticizer used in PVC compound restricts PVC in many medical applications. Special grade of TPV can be used for various medical application, however is opaque. Silicone tubing is very expensive. Medical grade SBC compounds have transparent or translucent appearance and are suitable for medical tubing applications.

Major requirements for medical tubing are listed:

Transparent or translucent
Kink resistance
Peristaltic pump life
Autoclavable/Gamma Sterilizable
Low extractable
Hardness and modulus requirement

The comparison of properties of SBC compound, PVC and TPV are listed in Table II. The PVC has a more than 30 percentage higher specific gravity than SBC compound. At same hardness, PVC and TPV have a much higher modulus and lower elongation than SBC compound. Therefore, SBC compound has a better "rubber" feeling than both PVC and TPV.

Stress and stain relation of the above four TPE is shown in Figure 4.

Summary

SBC compounds have been developed for silicone and PVC replacement. Their properties are compared with that of silicone and PVC. SBC compounds provide properties suitable for certain medical and personnel care applications, which currently mainly use silicone and PVC for performance and cost reasons.

Reference

1. Y. M. Lu and J. Kutka, Clear and Hight Hest Resistance TPEs, ANTEC, 2000.

Figure 1a. TEM of low molecular weight SEBS/Oil/PP compound

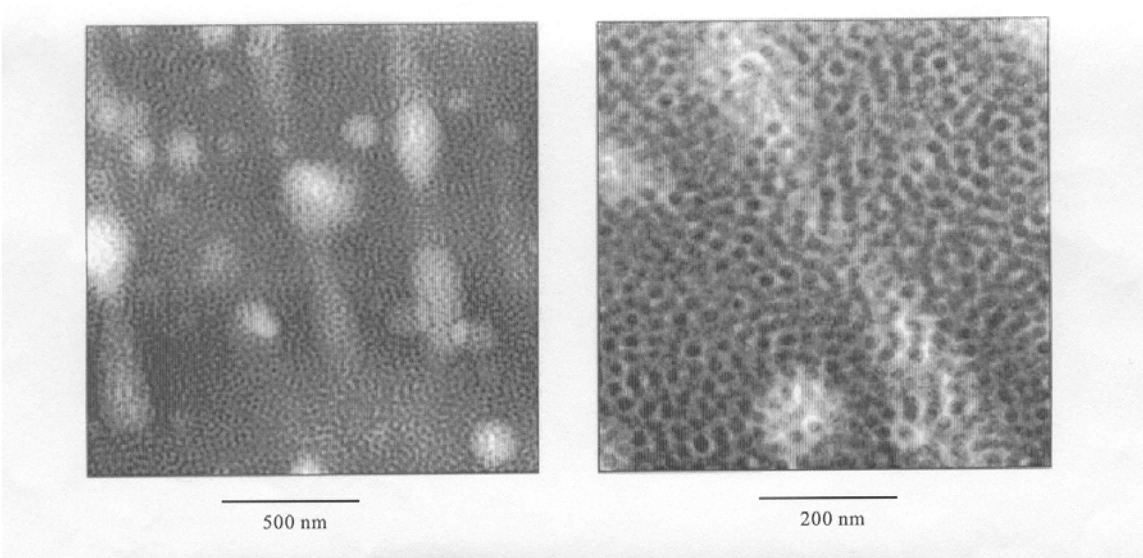

Figure 1b. TEM of high molecular weight SEBS/Oil/PP compound

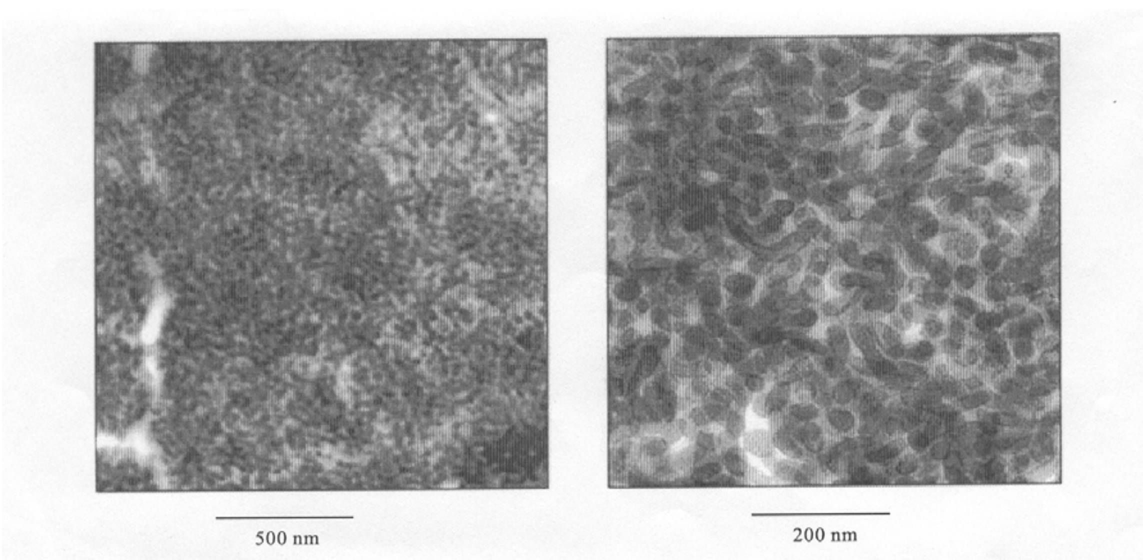

Figure 2. TMA strain versus temperature measurement

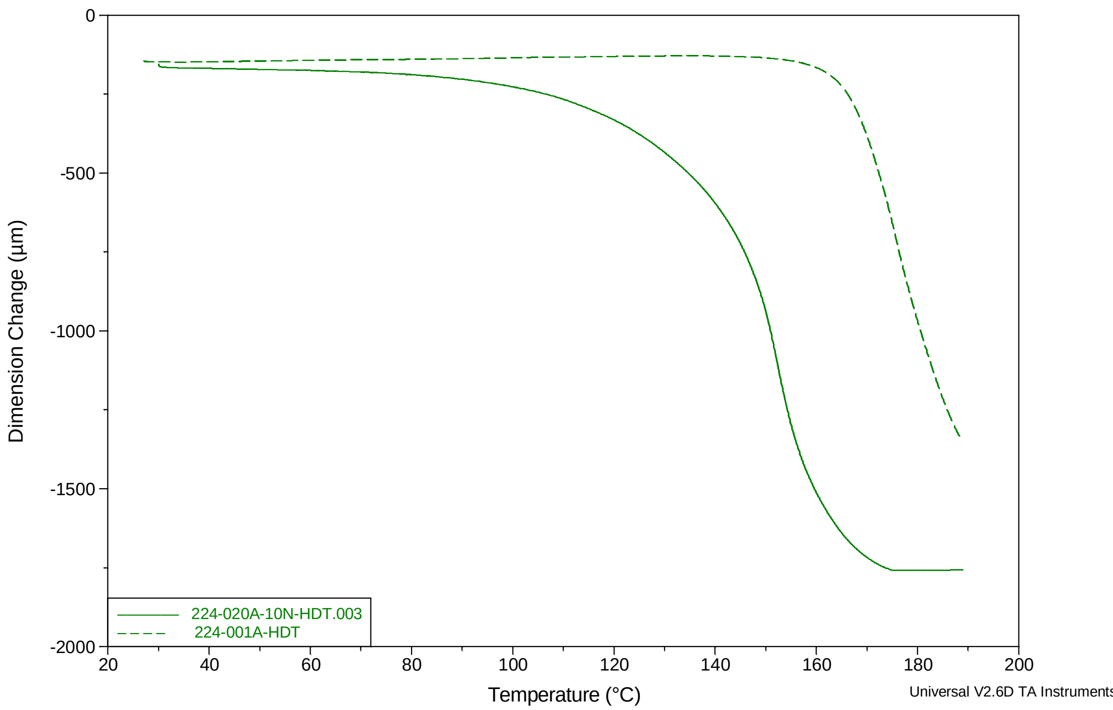

Figure 3. Stress versus strain of two SBC compound with similar tensile and elongation

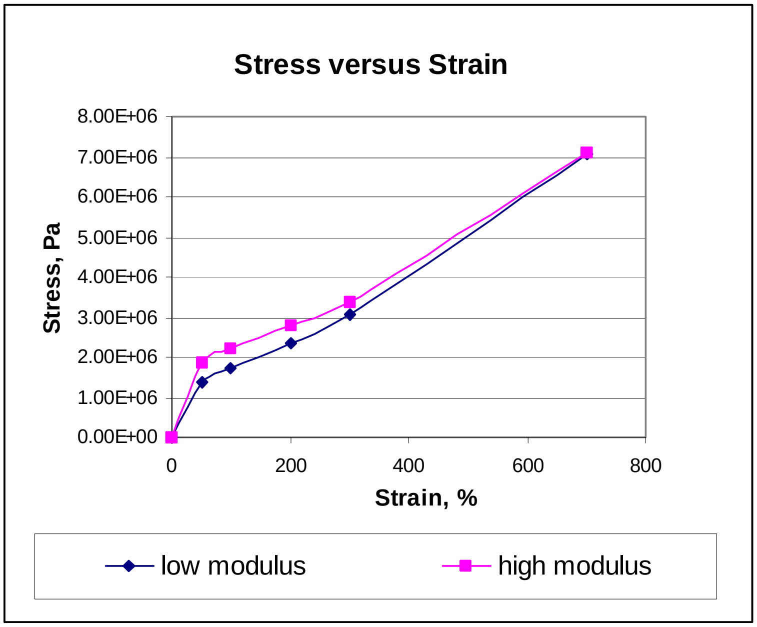

Figure 4. Stress versus strain of PVC, TPV and SBC compounds

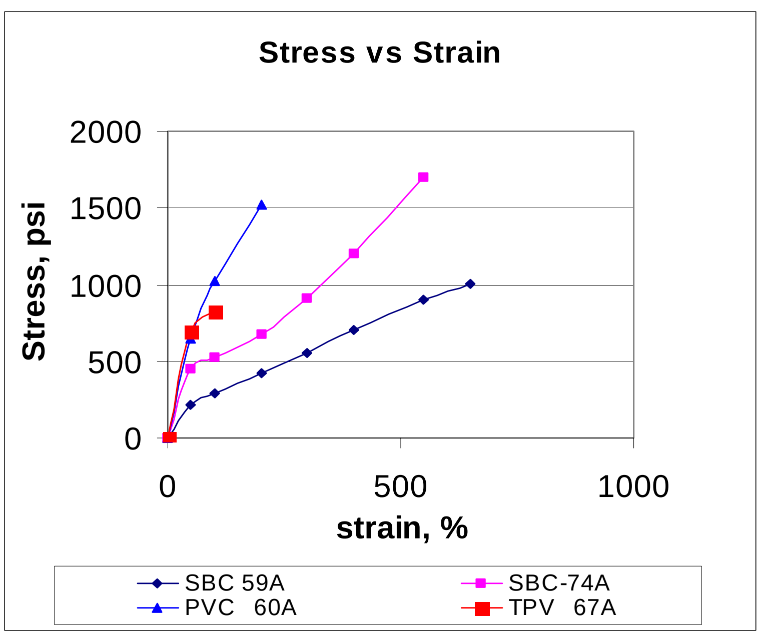

Table I Comparison of properties of silicone rubber and SBC compound

	Silicone Wacker 420/50S	SBC compound
Sp. Gravity	1.15	0.89
Ratio of specific gravity	1.29	1
Hardness, A	50	54
Tensile, Pa, 10^6 (psi)	8.96 (1300)	7.01 (1029)
Tear, N/M, 10^4 (lb/in)	3.20 (182)	3.22 (183)
Elongation, %	>500	690
Clarity	transparent	transparent
British tear test	passed	passed
Boiling water/dish washer	passed	passed

Table II Comparison of properties of SBC compound, PVC and TPV

	PVC-60 A	TPV-67A	SBC-59A	SBC-74A
Hardness, A	60	67	59	74
Specific gravity	1.20	0.97	0.90	0.90
100% modulus, Pa, 10^6 (psi)	7.07 (1025)	5.67 (822)	2.03 (295)	3.63 (527)
Tensile, Pa, 10^6 (psi)	9.65 (1400)	6.21 (900)	6.94(1007)	11.7(1700)
Tear, N/M, 10^4 (lb/in)	3.25 (185)	2.14 (122)	3.36 (192)	4.38 (250)
Elongation	250	150	650	550
Clarity	transparent	opaque	semi-transparent	transparent